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आपका किस्सा नहीं एक दिन कहानी बनेगी...!!

CSIR NET – Life Science

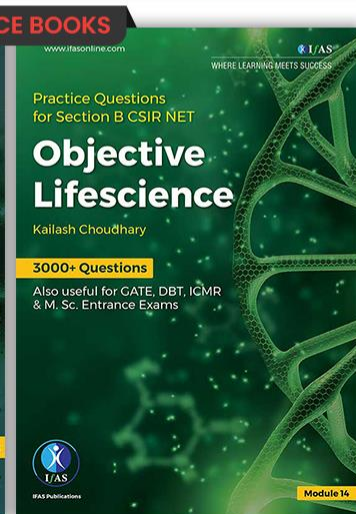
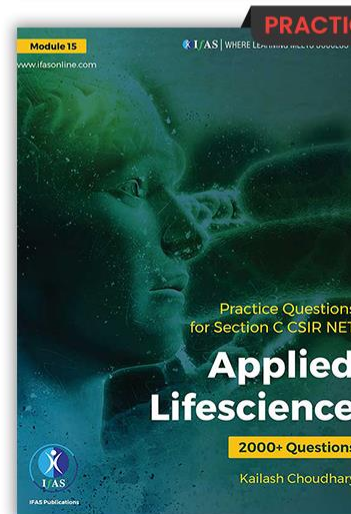
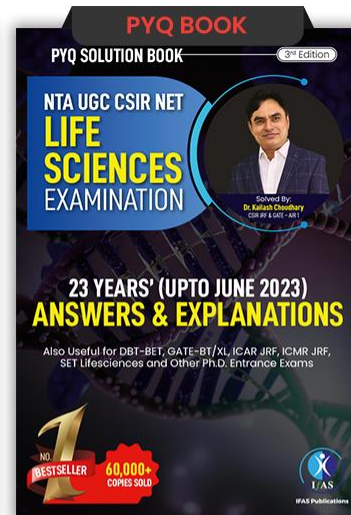
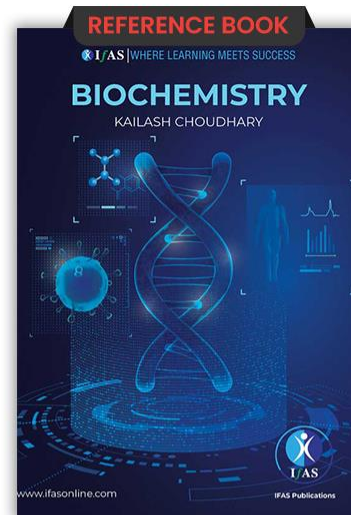
Unit 1: Biochemistry

05

Thermodynamics



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Points to be covered in this Lecture

 Laws of Thermodynamics Gibb's Helmholtz Equation Standard Gibb's Free Energy Chemical Equilibrium Coupled Reactions Energy Rich Molecule Group Transfer Cellular Gibbs Free Energy



What is Thermodynamics ?

- It is the study of energy transformations in any system.
- Energy is capability to do work
- Work = Force X displacement $w = F \cdot d$
- Work = Pressure X Change in Volume $w = P \Delta V$



UNITS OF ENERGY:

✓ **Calorie:** Amount of heat needed to raise the temperature of 1 gram of water by 1°C.
(energy)

✓ **Kilo Calorie:** Amount of heat needed to raise the temperature of 1 Kilogram of water by 1°C.

1 Kilocalorie = 1000 calorie

1 calorie = 4.184 Joules

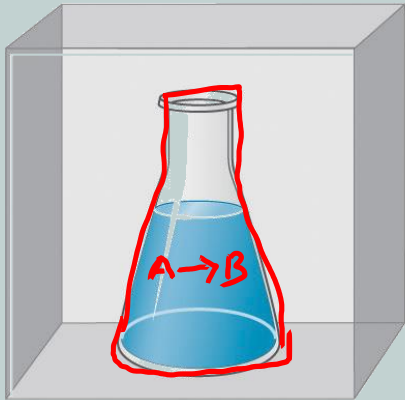
1 calorie = 4.2 Joule

calorie
Kilo calorie or Kcal or Cal

Universe = System + Surrounding

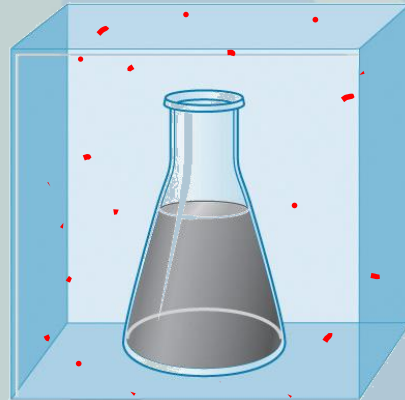
A system refers to the matter within a defined region of space.

The matter in the rest of the universe is called the *surroundings*.



System

+

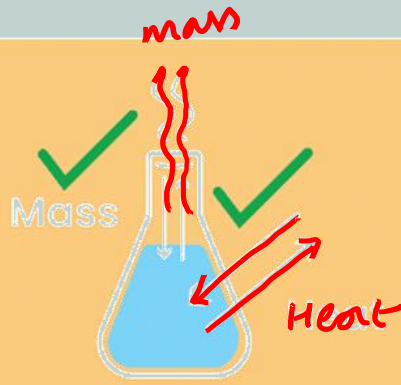


Surroundings

=

Universe

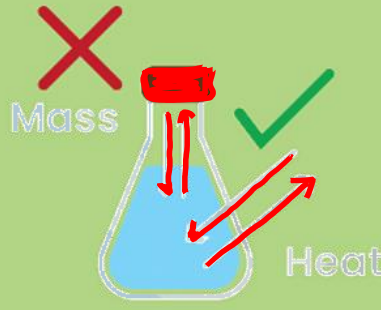
TYPES OF SYSTEM : Exchange of Heat (Energy) and mass (matter)



Open system

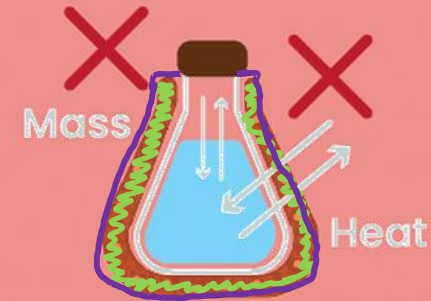
Exchange both 'Q' & mass with surrounding

- eg : Biological system.



Closed system

Exchange only energy to surrounding



Isolated system

Do not exchange energy or matter to surrounding

eg Universe
Thermus (temporary)

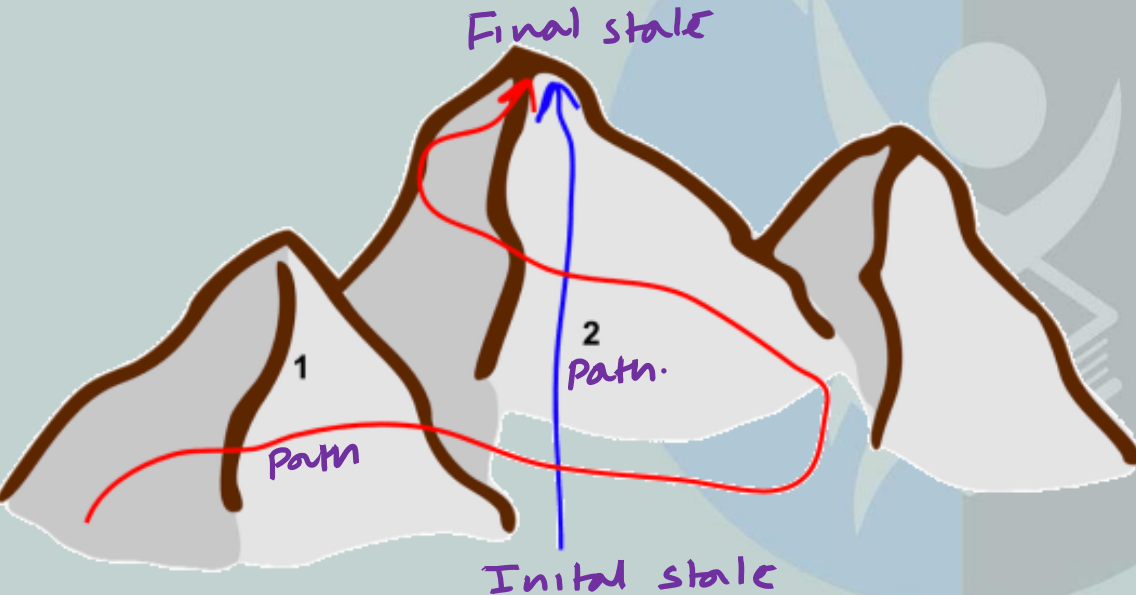


State function: Independent of path a system follows

- Pressure
- Enthalpy

Volume
Entropy

Internal Energy
Free energy



Path function Imp

Dependent of path a system follows

- Heat (Q)
- Work (w)

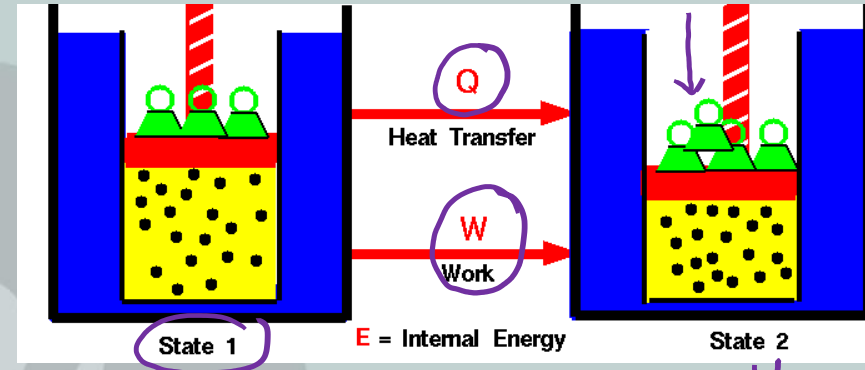


FIRST LAW : Law of conservation of energy

- The **total energy** of an universe is **constant**.
- Energy can be neither created nor destroyed in isolated system.
- Energy for biological system (open system) can increase or decrease

Internal energy (E or U)

- Energy contained in system



E of any system can change only if energy flows in or out of the system in the form of heat or work.

$$\Delta U = U_2 - U_1 = \pm q \pm W$$

$+q$ (gain) $+w$ (done on system)
 $-q$ (loss) $-w$ (done by system)

$$W = P \Delta V \text{ or } F \cdot d$$



APPLY YOUR MIND

The internal energy of a gas increases by 1J when it is compressed by a force of 1 Newton through 2 meters.

The heat change of the system is:

(1) 1 J

☒ (2) -1 J

(3) 2 J

(4) -2 J

$$U = +1 \text{ J}$$

$$F = 1 \text{ N}$$

$$D = 2 \text{ m}$$

$$W = F \times D = 1 \times 2 = 2$$

+W

$$U = Q + W$$

$$\begin{aligned} Q &= U - W \\ &= 1 - 2 \\ &= -1 \end{aligned}$$



Internal Energy (U):

$$U = Q \pm W$$

$$\boxed{\Delta U = \Delta Q}$$

$$\begin{aligned} \checkmark W &= P \Delta V \\ \Delta V &= 0 \\ W &= 0 \end{aligned}$$

The heat exchanged at constant volume

Enthalpy (H):

$$W = P \boxed{\Delta V}$$

Heat exchanged at constant pressure.

$$\underline{H} = \boxed{U} + \underline{P \Delta V}$$



Entropy (S)

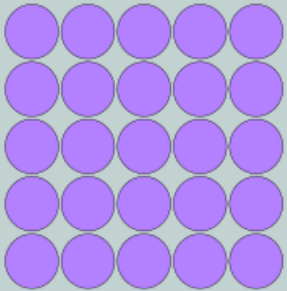
✓ Measure of randomness or disorderness

Thermal energy per unit temperature that is unavailable for doing useful work

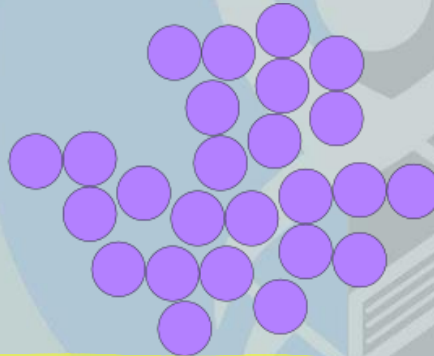
Q

T

✓ $S = \frac{Q}{T}$ ← $\frac{\text{Joule}}{\text{Kelvin}}$



Low Entropy



High Entropy



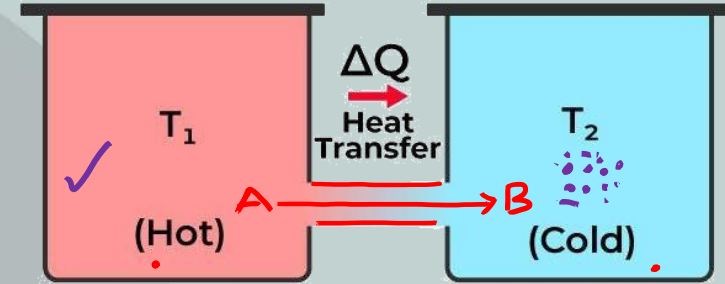
Second Law of Thermodynamics: Law of entropy

$A \longrightarrow B$

In any spontaneous process, the total entropy (degree of disorder or randomness) of a system and its surroundings always increases.
(universe)

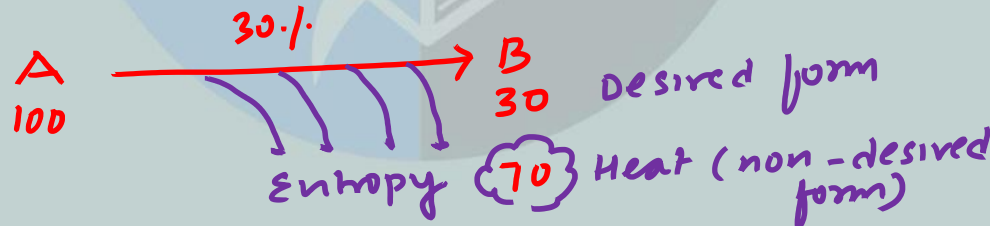
Entropy of system may increase or decrease but entropy of universe always increases.

Gives information about the efficiency of energy conversion



$$\Delta S = \text{Entropy} = \frac{\Delta Q}{T}$$

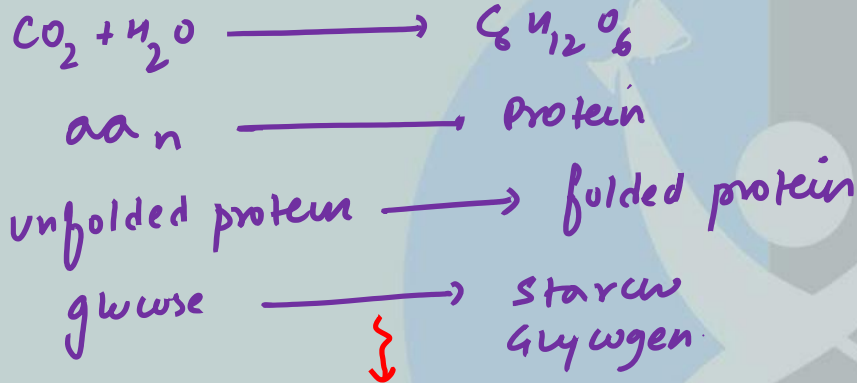
$$S = \frac{Q}{T}$$





Biological system are not exception to second law

Entropy = \downarrow



• Non-spontaneous

• System = entropy = \downarrow surrounding entropy = \uparrow
Net universe entropy = \uparrow i.e.

entropy = \uparrow

A \longrightarrow B

- Spontaneous
- Universe — system + surrounding

Example of open system



First Law:

$$\Delta H = (+)$$

$$\Delta H = (-)$$

Not Favorable/No

Favorable/Yes

Endothermic x

Exothermic ✓

$$\Delta n = -ve \text{ (yes)}$$

$$\Delta S = +ve \text{ (yes)}$$

$$\Delta n = +ve \text{ (no)}$$

$$\Delta S = -ve \text{ (no)}$$

$$\Delta H = +ve \text{ (no)}$$

$$\Delta S = (+)ve \text{ (yes)}$$

= ?

$$\Delta n = -ve \text{ (yes)}$$

$$\Delta S = -ve \text{ (no)}$$

= (?)

Second Law:

$$\Delta S = (+)$$

$$\Delta S = (-)$$

Favorable/Yes

Not Favorable/No

Disordemen = ↑

Disordemen = ↓

The Gibbs free energy:

* Energy available to do work

$$\Delta G = \Delta H - T\Delta S$$

ΔG : Total Energy
 ΔH : Total Energy
 $T\Delta S$: Non-usable Energy

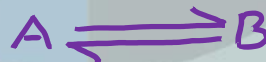
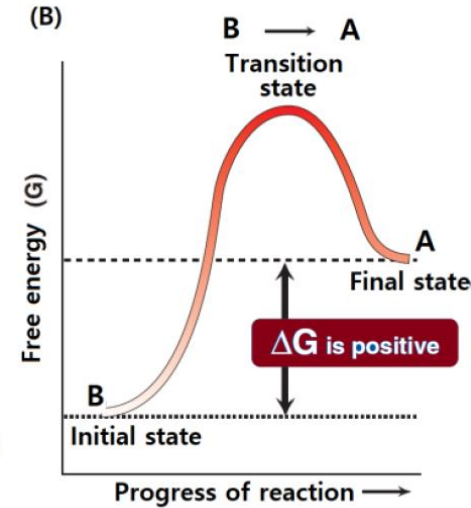
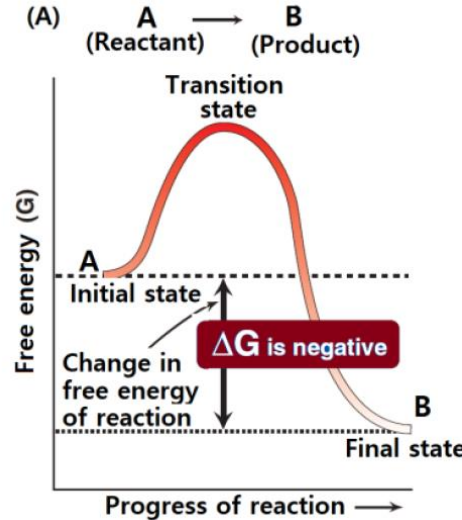
Gibb's Helmholtz Equation

$\Delta G = -$ Spontaneous, Favored in forward direction

$\Delta G = +$ Non-Spontaneous, Favored in backward direction

$\Delta G = 0$ Reaction is at equilibrium

* Direction of reaction can be predicted





If $\Delta G = 0$, means= equilibrium, Forward rate of reaction is equal to backward rate of reaction

$$\Delta H = T\Delta S$$



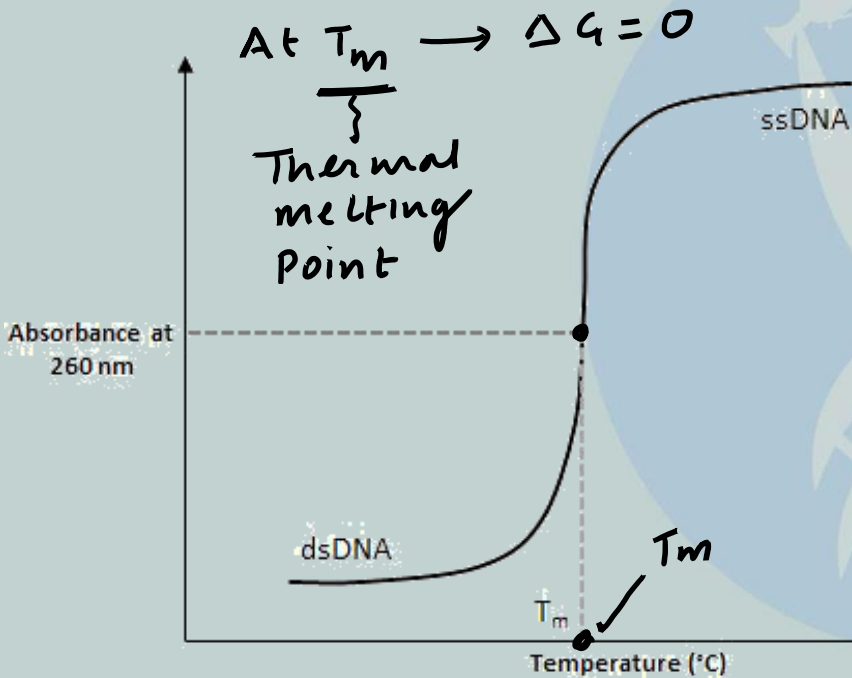
$$K_F = K_B \quad \Delta G = 0$$

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$\Delta H = T\Delta S$$

$$\Delta S = \frac{\Delta H}{T_m} = \frac{\Delta Q}{T}$$





Case A:

If ΔH = negative (yes)

ΔS = positive (yes)

$$\Delta G = \frac{\Delta H}{-} - T \frac{\Delta S}{+}$$

Diagram showing the signs in the equation: ΔH is negative (-), ΔS is positive (+), and the minus sign between them is highlighted with a bracket and an arrow pointing to the plus sign in the denominator of the second term.

Case B:

If ΔH = positive (NO)

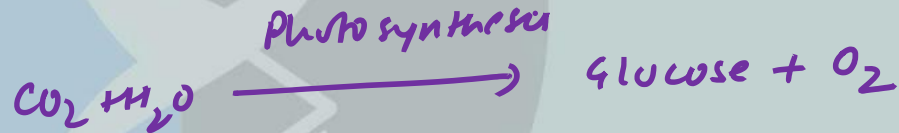
ΔS = negative (NO)

$$\Delta G = \frac{\Delta H}{+} - T \frac{\Delta S}{-}$$

Diagram showing the signs in the equation: ΔH is positive (+), ΔS is negative (-), and the minus sign between them is highlighted with a bracket and an arrow pointing to the plus sign in the denominator of the second term.



- ΔG will be always negative (regardless of Temp)
- Process is always spontaneous



- Non-spontaneous



Case C:

$$\Delta n = 10000$$

$$\Delta S = 25$$

$$T_m = \frac{10000}{25}$$

$$T_m = 400 \text{ K}$$

$$= 400 - 273^\circ$$

$$= 127^\circ \text{C}$$

If ΔH = Negative (Yes)

ΔS = Negative (No)

ΔG = Negative (Yes)

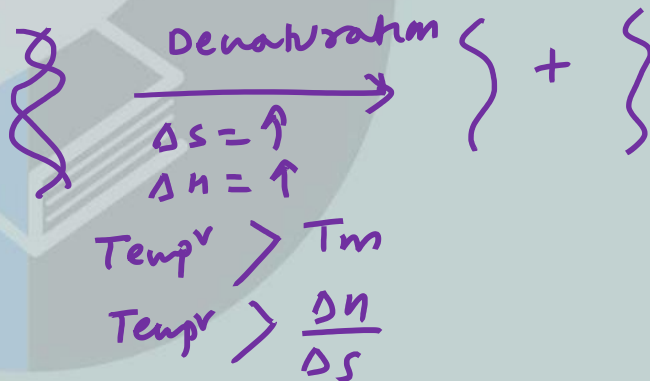
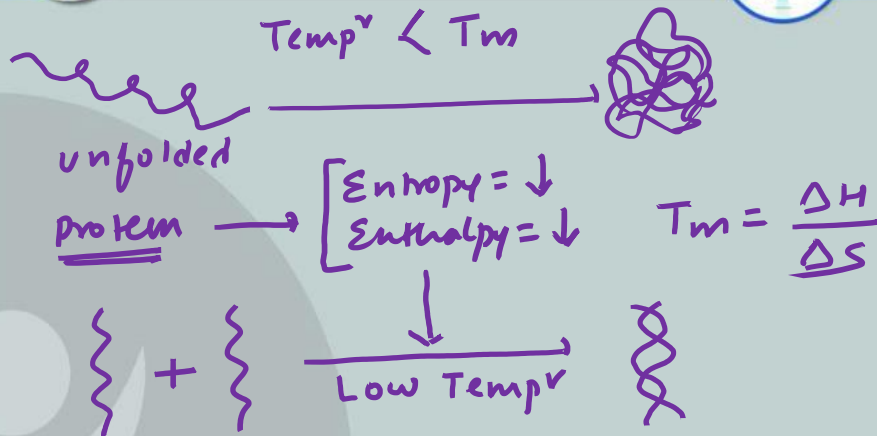
$$T < \frac{\Delta H}{\Delta S}$$

Case D:

If ΔH = Positive (No)

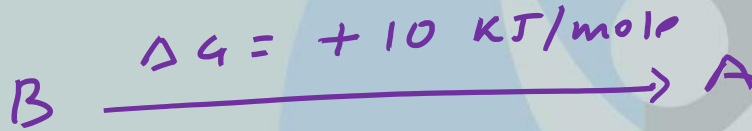
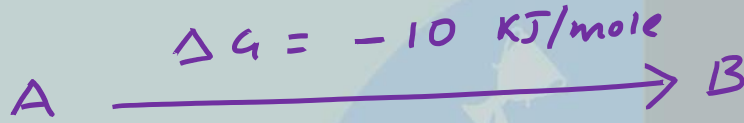
ΔS = Positive (Yes)

$$\Delta G = -ve \text{ (Yes)} \quad T > \frac{\Delta H}{\Delta S}$$





ΔG of the forward and backward reactions is same except sign





Imp

- ΔG does not provide information about rate of reaction
- Reaction rate depends on activation energy
- More Negative ΔG does not mean fast reaction
- More Negative ΔG mean reaction is more favored in forward direction
- Negative ΔG means product will be more than substrate at equilibrium

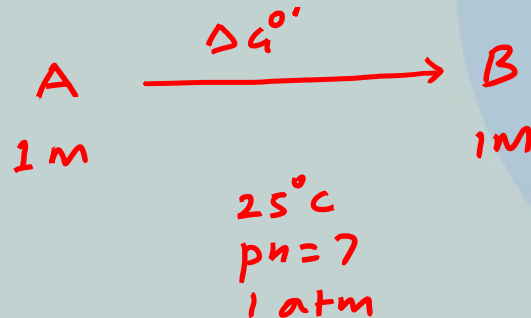




The Standard Gibbs free energy (ΔG^0)

Standard conditions

- Substate and product 1.0 M
- A temperature of 25 °C or 298 K
- A pressure of one atmosphere: 1 atm or 101.325 kPa,
- Water standard state: 55.5 M
- pH = 0 or pH = 7 (ΔG^0 or $\Delta G^{0'}$)

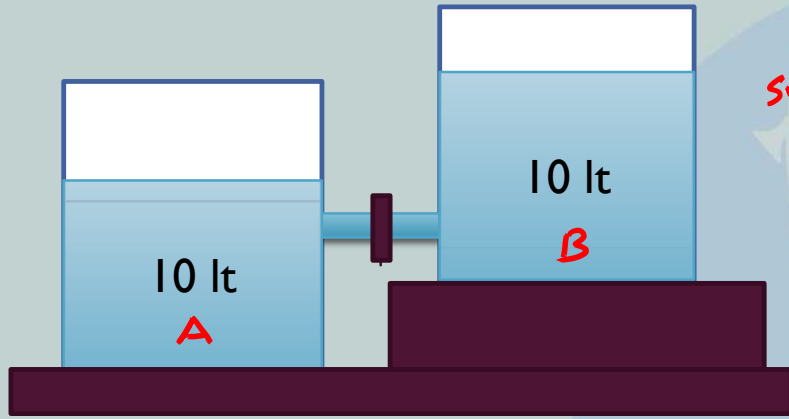


$$\underline{\Delta G^0} = \underline{\Delta H^0} - T \underline{\Delta S^0}$$



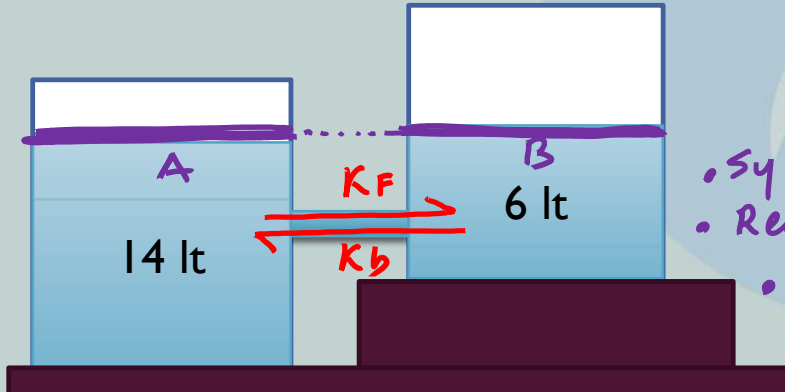
Chemical equilibrium:

$$K_{eq} = [P]/[S]$$



system is not at equilibrium

$$K_{eq} = \frac{(\text{product})}{(\text{substrate})} = \frac{K_F}{K_b}$$

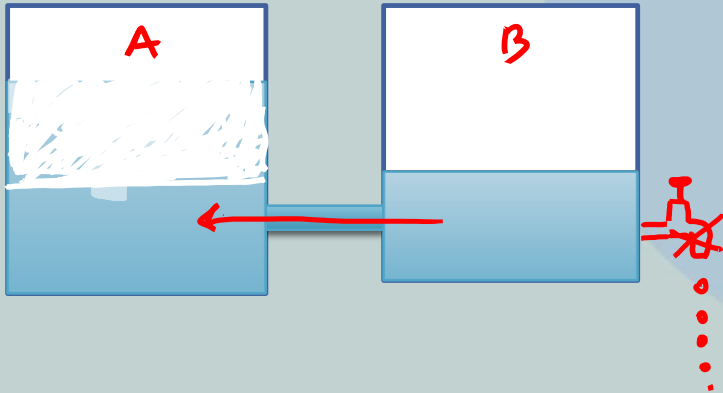


- system is at equilibrium
- Reaction completed
- No change in concⁿ.



Le Châtelier's Principle:

Any deviation from equilibrium stimulates a process that tends to restore the system to equilibrium.



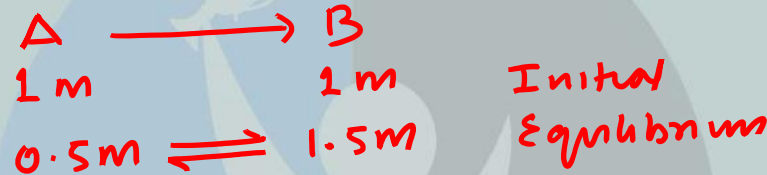


- K_{eq} can be more than 1, less than 1 or 1
- Standard free energy can be predicted by K_{eq}

$$K_{eq} = \frac{(P)}{(S)}$$

$$\frac{K}{K_{eq}} = \frac{K_F (P)}{K_0 (S)}$$

Equilibrium



$$K_{eq} = \frac{1.5}{0.5} = 3$$

$$K_{eq} > 1 \quad \Delta G = -ve$$

$$K_{eq} < 1 \quad \Delta G = +ve$$

$$K_{eq} = 1 \quad \Delta G = 0$$

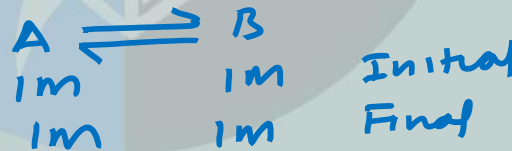
Spontaneous

Non-spontaneous



Initial $K_{eq} = \frac{0.5}{1.5}$

Final $K_{eq} = \frac{1}{3} = 0.33$





Relationship between K_{eq} and ΔG^0

$$\Delta G^0 = -RT \ln K_{eq}$$

$$\Delta G^0 = -2.303 RT \log K_{eq}$$

$$\Delta G^0 = -1363 \log K_{eq} \quad (\text{cal/mole})$$

$$R = 1.987$$

$$T = 298$$

$$\Delta G^0 = -1.36 \log K_{eq} \quad (\text{for answer in Kcal/mole})$$

$$\Delta G^0 = -5.7 \log K_{eq} \quad (\text{for answer in KJ/mole})$$

$$K_{eq} > 1$$

$$\Delta G^0 < 0 \quad (-ve)$$

$$K_{eq} < 1$$

$$\Delta G^0 > 0 \quad (+ve)$$

$$K_{eq} = 1$$

$$\Delta G^0 = 0$$



K_{eq}	$\log K_{eq}$	ΔG_o (kcal.mol ⁻¹)	ΔG_o (kJ.mol ⁻¹)
1000000 (10 ⁶)	6	-8.17	-34.3
100000 (10 ⁵)	5	-6.81	-28.5
10000 (10 ⁴)	4	-5.45	-22.8
1000 (10 ³)	3	-4.08	-17.1
100 (10 ²)	2	-2.72	-11.4
10 (10 ¹)	1	-1.36	-5.7
1 (10 ⁰)	0	0	0
0.1 (10 ⁻¹)	-1	+1.36	+5.7
0.01 (10 ⁻²)	-2	+2.72	+11.4
0.001 (10 ⁻³)	-3	+4.08	+17.1
0.0001 (10 ⁻⁴)	-4	+5.45	+22.8
0.00001 (10 ⁻⁵)	-5	+6.81	+28.5
0.000001 (10 ⁻⁶)	-6	+8.17	+34.3

$$K_{eq} = 100$$

$$\Delta G^\circ = -1.36 \log K \quad \frac{\text{K. cal}}{\text{mole}}$$

$$= -1.36 \log 100$$

$$= -1.36 \times 2$$

$$\Delta G^\circ = -2.72 \quad \frac{\text{K. cal}}{\text{mole}}$$



Apply your mind:

Equilibrium constant (K) of noncovalent interaction between two non-bonded atoms of two different groups was measured at 27°C . It was observed that $K = 100 \text{ M}^{-1}$. The strength of this noncovalent interaction in terms of Gibbs free energy change is:

(1) ~~$\times 2.72 \text{ Kcal/mole}$~~

(2) $\ominus 2.72 \text{ Kcal/mole}$

(3) ~~$\times 0.27 \text{ Kcal/mole}$~~

(4) $\ominus 0.27 \text{ Kcal/mole}$

$$\begin{aligned} & \boxed{K=100} \quad K > 1 \quad \Delta G^\circ = -ve \\ \Delta G^\circ &= -1.36 \log K \quad (\text{K cal/mole}) \\ &= -1.36 \log 100 \\ &= -1.36 \times 2 \\ &= -2.72 \end{aligned}$$



Apply your mind:

Equilibrium constant (K'_{eq}) of reaction is a ratio of product to substrate concentration. The reaction between (K'_{eq}) and free energy change in a reaction ($\Delta G'$) is follows

$$\Delta G' = -RT \ln K'_{eq}$$

Reaction A and reaction B have K'_{eq} values of 10 and 100, respectively. Which of the following statement is correct with respect to $\Delta G'$?

- (1) $\Delta G'$ of A = $\Delta G'$ of B
- ☒ (2) $\Delta G'$ of A > $\Delta G'$ of B
- (3) $\Delta G'$ of B > $\Delta G'$ of A
- (4) $\Delta G'$ of A \approx $\Delta G'$ of B

A		B
$K = 10$		$K = 100$
$\Delta G^\circ = -1.36 \log K$		$\Delta G^\circ = -1.36 \log K$
$= -1.36 \log 10$		$= -1.36 \log 100$
$= -1.36 \times 1$		$= -1.36 \times 2$
$\Delta G_1^\circ = \underline{-1.36}$	>	$\Delta G_2^\circ = \underline{-2.72}$



Apply your mind:

$\left\{ \begin{matrix} 310 \text{ K} \\ 298 \text{ K} \end{matrix} \right\} \leftarrow \text{Ignore}$

ΔG° for the base pairing of five oligonucleotides at 300 K is $-17.1 \text{ kJ mol}^{-1}$. What would be the approximate value of the equilibrium constant K ?

(1) 100 ~~X~~ -11.4

~~X~~ (2) 10 -5.7

☒ (3) 1000 -17.1

(4) 1 ~~X~~ 0

$K > 1$

$$\Delta G^\circ = -2.303 RT \log K$$

$$\Delta G^\circ = -5.7 \log K$$

$$-17.1 = -5.7 \log K$$

$$\frac{-17.1}{-5.7} = \log K$$

$$3 = \log K$$

$$\text{Antilog } 3 = K$$

$$1000 = K$$



Standard free energy change in molecular interactions:

K_{eq} ↘

- Dissociation constant (K_d) : Free Energy during dissociation $\Delta G^\circ = -2.303 RT \log K_d$
- Binding or association constant (K_a) : Free Energy during binding

$$\hookrightarrow \Delta G^\circ = -2.303 RT \log K_a$$

$$K_d = \frac{1}{K_a}$$



Apply your mind

The Gibbs free energy of binding of a ligand with a protein is determined using calorimetric measurements at 25°C. The value of ΔG° thus determined is +2.72 kcal/mole. The binding constant for the ligand-protein association is:

- (1) 0.01
(3) 1.00 X

(K_a)

- (2) 0.10
(4) 100 X

$$\Delta G^\circ = (+)$$

$$K_{eq} < 1$$

$$\begin{aligned}\Delta G^\circ &= -1.36 \log 0.01 \\ &= -1.36 \log 10^{-2} \\ &= -1.36 \times -2 \\ &= +2.72\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= -1.36 \log 0.1 \\ &= -1.36 \log 10^{-1} \\ &= -1.36 \times -1 \\ &= +1.36\end{aligned}$$



van't Hoff Equation

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$\Delta G^{\circ} = -RT \ln K_{eq}$$

$$-RT \ln K_{eq} = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$RT \ln K_{eq} = \overbrace{-(\Delta H^{\circ} - T \Delta S^{\circ})}$$

$$RT \ln K_{eq} = -\Delta H^{\circ} + T \Delta S^{\circ}$$

$$\ln K_{eq} = \frac{-\Delta H^{\circ} + T \Delta S^{\circ}}{RT}$$

$$\ln K_{eq} = \frac{-\Delta H^{\circ}}{RT} + \cancel{\frac{T \Delta S^{\circ}}{RT}}$$

$$\ln K_{eq} = \frac{-\Delta H^{\circ}}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^{\circ}}{R}$$

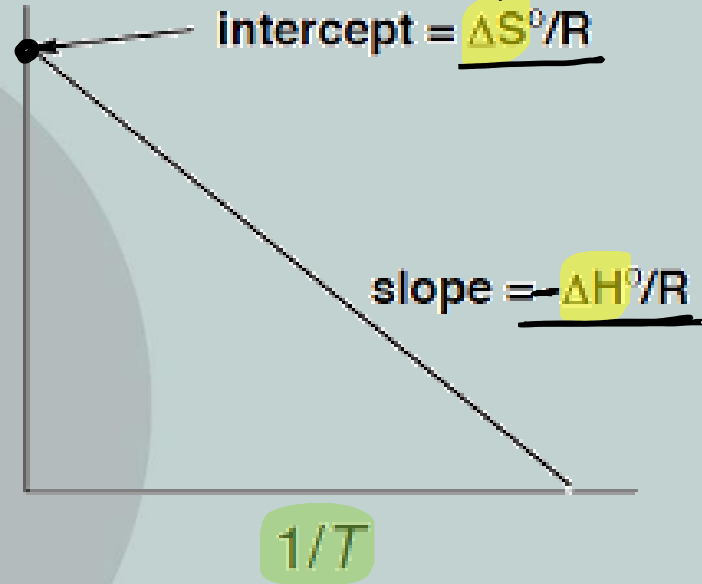


Van't Hoff Plot

$$\ln K_{eq} = \frac{-\Delta H^0}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^0}{R}$$

$$Y = m \cdot x + c$$

\uparrow Slope (Enthalpy)
 \uparrow y-axis Intercept (Entropy)

 $\ln K_{eq}$




Apply your mind:

Protein stability is represented as (JUNE 2017)



Prior to development of sensitive calorimeters, thermodynamic parameters of processes were determined by following equation

$$\ln K_{eq} = \frac{-\Delta H^0}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^0}{R}$$

$$y = m \cdot x + c$$

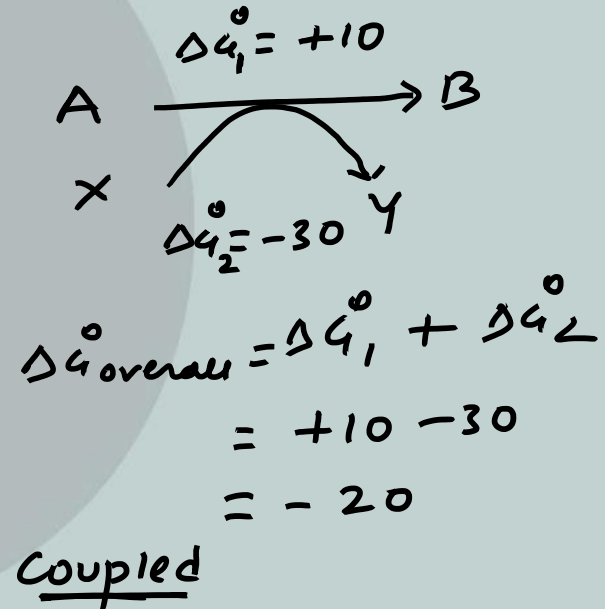
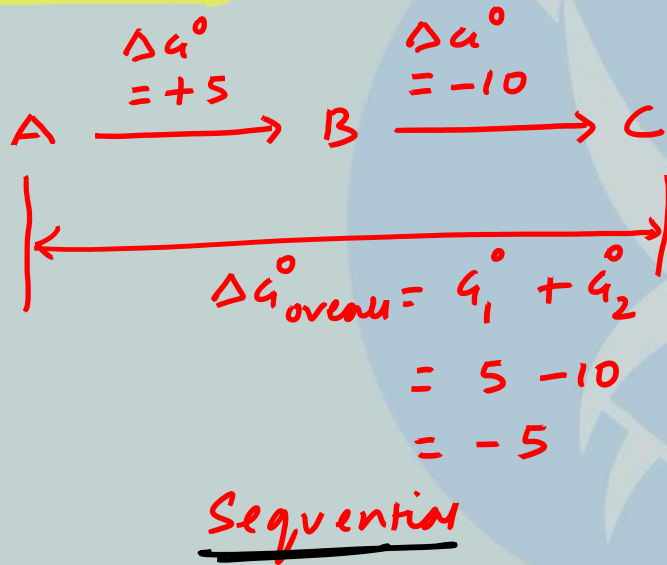
ΔH^0 and ΔS^0 are standard changes in enthalpy and entropy, respectively. Which one of the following statements is correct for estimating ΔG , ΔH and ΔS ?

- (1) Determining the ratio of folded & unfolded protein at 37°C
- (2) Plotting K_{eq} as a function of ΔH
- (3) Plotting K_{eq} against ΔS
- (4) Plotting K_{eq} against temperature



Sequential and coupled reactions

Standard free-energy changes are additive for sequential and coupled reactions

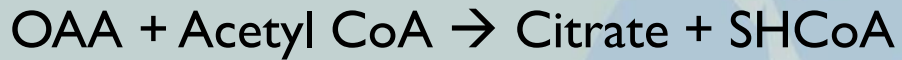




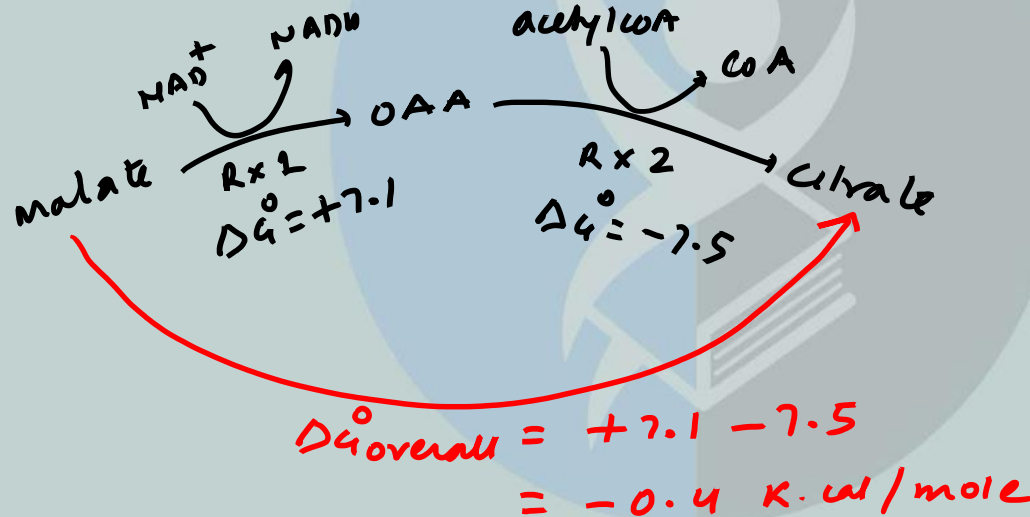
Sequential reactions



$$\Delta G^0 = +7.1 \text{ kcal/mole}$$

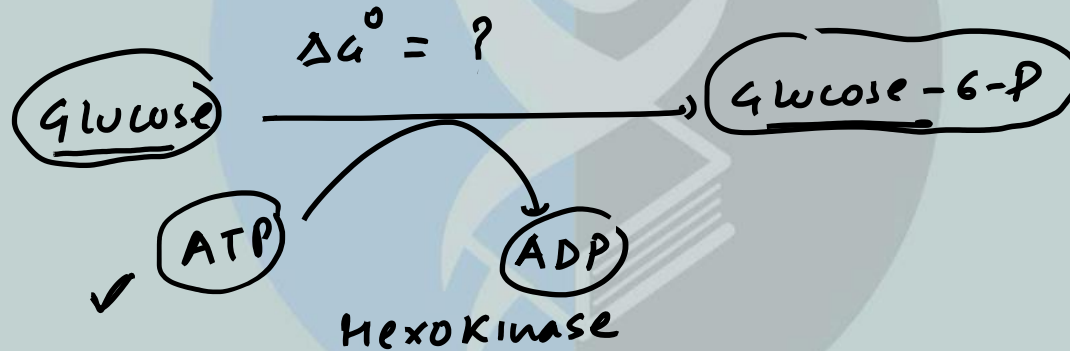
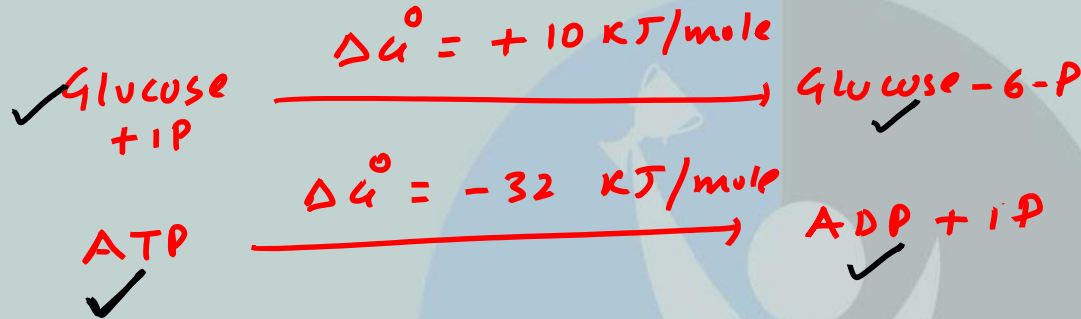


$$\Delta G^0 = -7.5 \text{ kcal/mole}$$





Coupled reactions



$$\Delta G^{\circ}_{\text{overall}} = \Delta G^{\circ}_1 + \Delta G^{\circ}_2 \\ (+10) + (-32) = -22 \text{ kJ/mole}$$



Apply your mind:

The reaction of glutamate and ammonia to glutamine and water has a value of $+14 \text{ kJ mol}^{-1}$ for ΔG° . This is coupled with the ATP reaction ($\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{phosphate}$). The ΔG° for this reaction is -30 kJ mol^{-1} .

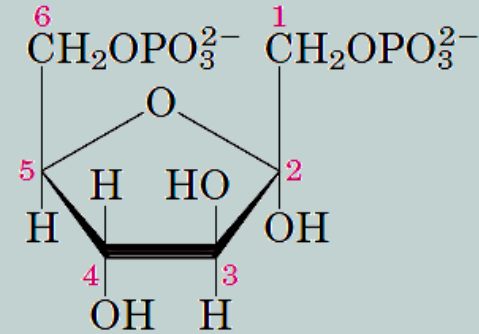
The ΔG° (KJ mol^{-1}) for the coupled reaction
 $\text{Glutamate} + \text{NH}_3 + \text{ATP} \rightarrow \text{Glutamine} + \text{ADP} + \text{Phosphate}$
under equilibrium condition is (JUNE 2014)

- (1) 16
- ✓ (3) -16

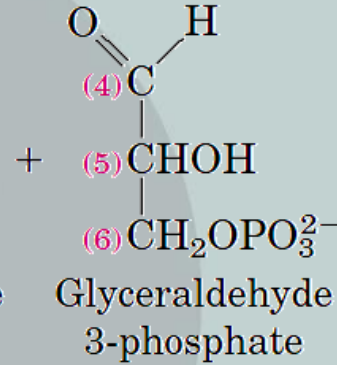
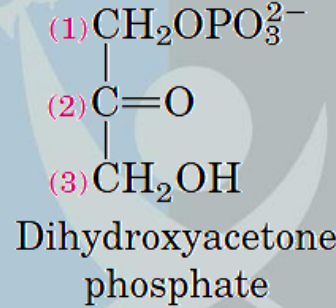
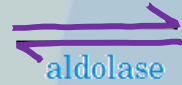
- (2) -44
- (4) 44

$$\begin{aligned} &= \Delta G^\circ_1 + \Delta G^\circ_2 \\ &= (+14) + (-30) \\ &= +14 - 30 \\ &= -16 \end{aligned}$$

ΔG^0 do not predict direction (spontaneously) of reaction under cellular conditions



Fructose 1,6-bisphosphate



$$\Delta G'^0 = 23.8 \text{ kJ/mol}$$

Predict only if standard conditions are given.

Cellular condition \rightarrow Forward/backward? \rightarrow cannot be predicted.
Depends on actual concⁿ of substrate & product



Actual free-energy (ΔG) changes depend on reactant and product concentrations under physiological conditions

$$\Delta G = \Delta G^\circ + 2.303 RT \log \frac{(\text{Product})}{(\text{Substrate})} \quad \left. \vphantom{\frac{(\text{Product})}{(\text{Substrate})}} \right\} \text{cellular concn}$$

$$\Delta G = \Delta G^\circ + \frac{(1.36)}{1.4} \log \frac{(P)}{(S)} \quad \text{K.cal/mole}$$

$$\Delta G = \Delta G^\circ + 5.7 \log \frac{(P)}{(S)} \quad \text{KJ/mole}$$

$$\Delta G = \Delta G^\circ + \frac{(1363)}{1400} \log \frac{(P)}{(S)} \quad \text{cal/mole}$$

$$\Delta G = \Delta G^\circ + 5700 \log \frac{(P)}{(S)} \quad \text{J/mole}$$



Apply your mind:

The standard free energy change (ΔG°) per mole for the reaction $A \rightarrow B$ at 30°C in an open system is -1000 cal/mole. What is the approximate free energy change (ΔG) when the concentration of A and B are 100 micromolar and 100 millimolar, respectively? (JUNE 2016)

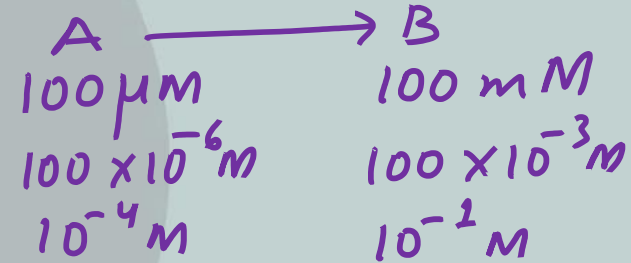
(1) 3160

(3) 31610

(2) 316

(4) -3160

$$\begin{aligned}\Delta G &= \Delta G^\circ + 1400 \log \frac{(P)}{(S)} \\ &= (-1000) + 1400 \log \frac{10^{-1}}{10^{-4}} \\ &= -1000 + 1400 \log 10^3 \\ &= -1000 + 1400 \times 3 \\ &= -1000 + 4200 = \boxed{+3200}\end{aligned}$$

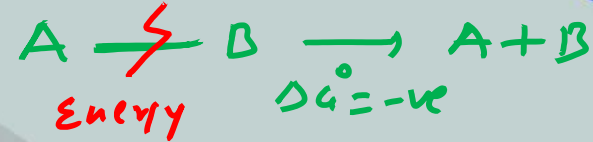


1.4 K · cal/mol

1400 cal/mole



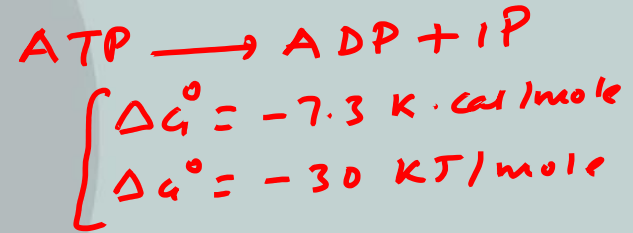
What are energy rich molecules/compounds?



✓ Molecules have bonds that, when broken, release a significant amount of energy.

✓ When hydrolysed, produce free energy that is greater or equal to that of ATP

ΔG is -7.3 kcal/mol or -30 KJ/mol or more negative



Example:

- ATP, GTP, CTP, UTP (NTP)
- PEP, 1,3 Bis Phosphoglycerate
- Carbamoyl Phosphate, Creatine Phosphate
- Succinyl CoA, Acetyl CoA

Group transfer Potential

Compound	ΔG° (Kcal/mol)
High Energy Bonds	
1. Phosphoenolpyruvate	-14.8
2. Carbamoyl phosphate	-12.3
3. 1,3-Bisphosphoglycerate	-11.8
4. ATP (\rightarrow AMP + PPi)	-10.9
5. Phosphate creatine	-10.3
6. Acetyl phosphate	-10.1
7. Arginine phosphate	-8.0
8. Acetyl CoA	-7.5
9. ATP (\rightarrow ADP + Pi)	-7.3
Low Energy bonds	
1. Glucose 1-phosphate	-5.0
2. Pyrophosphate (\rightarrow 2Pi)	-4.0
3. Fructose 6-phosphate	-3.8
4. AMP (\rightarrow Adenosine + Pi)	-3.4
5. Glucose 6-phosphate	-3.3
6. Glycerol 3-phosphate	-2.2

PEP: enol phosphate
 KJ/mole
 ATP: 2 energy rich bonds
 AMP ADP

Energy rich molecule

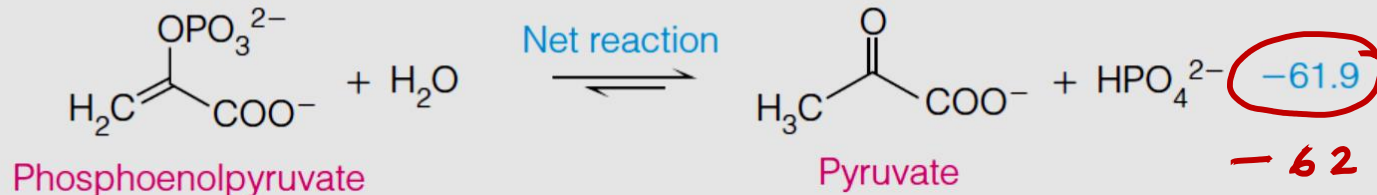
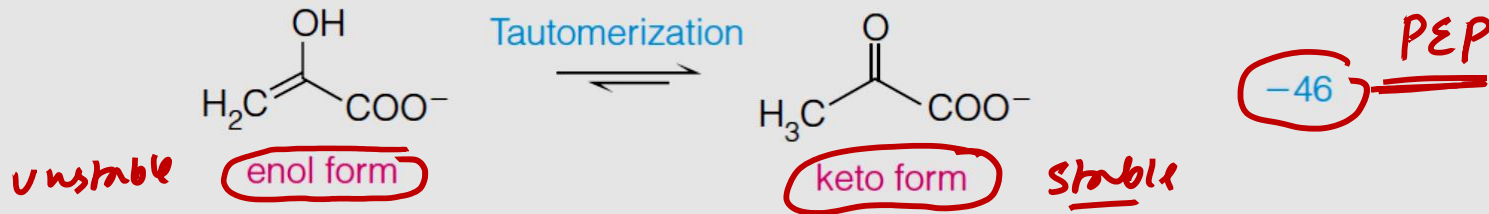
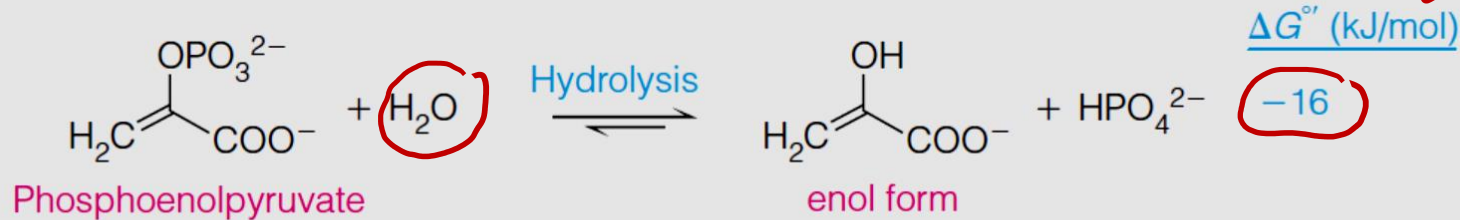
acetyl-CoA
 Succinyl-CoA

Thioester energy rich bond

KJ/mole
 not energy rich



Chemical basis for large free energy change with PEP hydrolysis



- 62 kJ/mole
- 14.8 kcal/mole

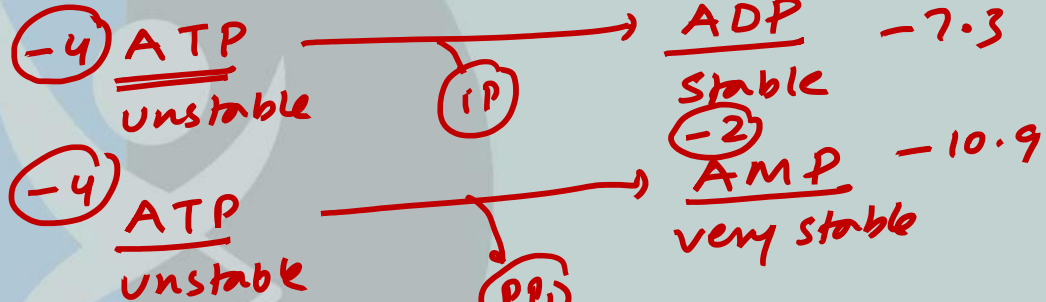
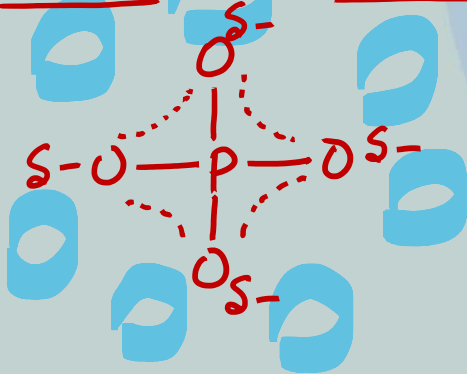
PEP is highly unstable and products are very stable

PEP \longrightarrow Pyruvate

Chemical basis for large free energy change with ATP hydrolysis

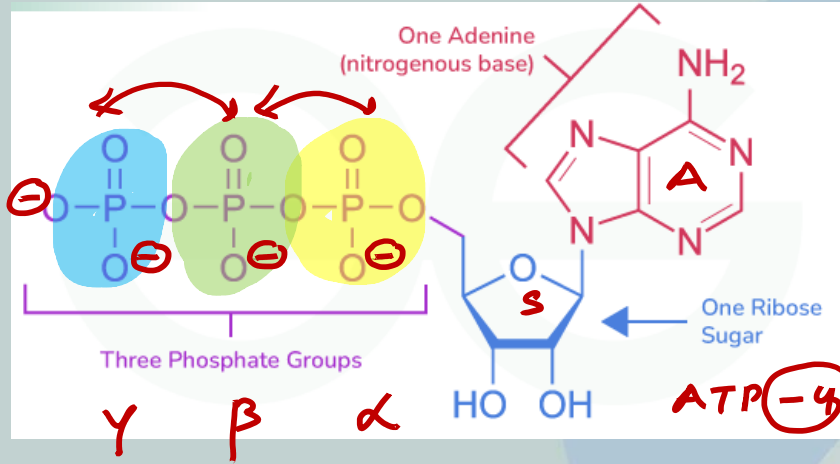


- ✓ Charge repulsion in substrate
- ✓ Resonance stabilization of product
- ✓ Hydration stability of products
- ✓ Ionization favors forward reaction



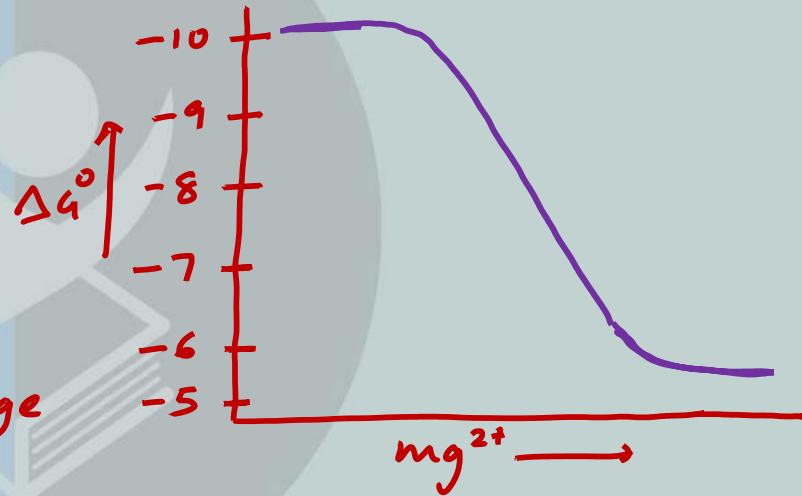


✓ Effect of Mg^{2+} on free energy of ATP hydrolysis



$Mg^{2+} \rightarrow$ Neutralize -ve charge of ATP
 \rightarrow Increase stability
 \rightarrow Lesser dissociation
 $\rightarrow \Delta G^\circ =$ lesser negative

ATP energy rich bonds = 2
 Acid anhydride bond





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